

Chemical Mapping of the Sea-Surface Microlayer: A System for Measurement of Spatial and Temporal Variations in Composition

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LONG-TERM GOALS

The viscoelastic behavior of the air-sea interface, a key parameter affecting air-sea exchange of mass, momentum and heat, is strongly dependent on naturally-occurring adsorbed surfactant materials (Frew, 1997; Frew *et al.*, 2002a). The long-term goals of this work are to understand the relationship between the composition of surface-active organic matter in the marine microlayer and the viscoelasticity of the sea surface and to delineate the role of microlayer films in modulating roughness and near-surface turbulence.

OBJECTIVES

The occurrence, spatial distribution, concentration and composition of sea surface films are not well known. In order to understand and model the impact of the surface microlayer on air-sea exchange processes, it is useful to have detailed information about the following:

- film formation rates and persistence as a function of wind stress;
- patchiness of film distributions over a range of spatial scales (10m – 1 km);
- surface tension and elasticity variations on these spatial scales;
- film composition as a function of film pressure, wind stress, and seasonal factors.

In order to develop such information, this project focuses on designing and deploying systems to detect and measure organic analytes in the marine microlayer in near-real time. Responding to a broad range of organic compounds, such systems can provide specific information on the composition and structure of surface-active materials and estimates of surface enrichments of specific surfactants that control the viscoelasticity of the sea surface.

APPROACH

A new survey tool, SCIMS (Slick Chemical Identification and Measurement System), which detects the presence of surface microlayer films and allows mapping their spatial and temporal distributions, is

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being deployed for seasonally distributed observations at the Marthas Vineyard Coastal Observatory (MVCO) off Cape Cod. SCIMS consists of a surface microlayer skimmer that is coupled to a fluorometry package and an automated extraction interface. It is used in conjunction with innovative ion trap mass spectrometry technology to study microlayer film accumulations and their specific composition. Deployed on a remotely piloted catamaran, SCIMS processes the skimmer flow stream, carrying out cyclical, microscale solid-phase extraction, concentration, desalting, and elution of microlayer surface-active organics for short-term archiving in an autosampler-compatible vial array. The time-series ‘snapshots’ of the extracted microlayer are then processed by a shipboard ion trap mass spectrometer (ITMS) to develop the surface compositional profile of the area surveyed by the skimmer, with a temporal resolution of about ten minutes. The mass spectral information can be further used with elasticity data to develop correlative relationships between film composition and elasticity. SCIMS also provides real-time measurements of microlayer and subsurface colored dissolved organic matter (CDOM) fluorescence with 1-second resolution.

WORK COMPLETED

During the current funding period, a series of SCIMS deployments at the Martha’s Vineyard Coastal Observatory (MVCO) site was initiated to look at surface film variations both spatially (10 meters – 10 km) and temporally (typically time scales of a few hours, but also over longer seasonal time scales). Several of these coincided with the August 2002 CBLAST-LOW Intensive Operating Period. SCIMS has now logged ~ 40 hrs of microlayer/subsurface CDOM fluorescence at the MVCO site and collected ~120 microlayer and subsurface surfactant samples. The fluorescence data from these deployments have been processed to provide estimates of microlayer surface excess CDOM. Film surface pressures have been estimated from the ambient surface tension, salinity and temperature data. Gibbs static elasticities (ϵ_0) have been computed from surface pressure-elasticity relationships. Roughly 10% of the SCIMS extracts have been examined by electron impact and electrospray mass spectrometry.

RESULTS

Analysis of the data from the SCIMS deployments at MVCO shows that this coastal environment is significantly impacted by surface films over the full range of wind stress conditions under which SCIMS can operate ($U_{10} < 7$ m/s). This was evident from observed surface excess CDOM distributions and depressed levels of surface tension. Microlayer CDOM fluorescence was normalized to the fluorescence of quinine sulfate (q.s.) standards (Vodacek *et al.*, 1997) and compared with bulk CDOM fluorescence. The latter generally averaged 1-1.5 ppb q.s. over the early summer-fall seasons. Surface chemical enrichments, as represented by differences in surface microlayer and subsurface concentrations of CDOM (Δ CDOM), were extremely variable, ranging from 2-250% of bulk CDOM concentration. Film surface pressures were generally 1-2 mN/m but reached levels as high as 25 mN/m in regions of highest Δ CDOM. Histograms of Δ CDOM for four individual SCIMS deployments are shown in Figure 1, arranged in order of increasing wind speed. The histograms illustrate the general tendency for Δ CDOM to adjust to the steady state wind stress. In very low winds, Δ CDOM distributions were very broad; films became highly patchy with slick features varying in scale from tens to hundreds of meters. Surface enrichments generally were not correlated with variations in subsurface CDOM. Thus, other processes, perhaps subsurface flows or buoyant overturning tended to dominate at low wind speeds and contribute to the enhanced inhomogeneity in surface coverage. As winds increased to moderate levels, the sea surface exhibited lower, more uniform surfactant film coverage and narrower Δ CDOM distributions. Several processes may

contribute to the erosion of films as winds increase, including dissolution into the bulk with increased surface straining, film disruption and downmixing by breaking waves, and increasing lateral advection due to the surface drift velocity. These processes can erode films fairly rapidly. However, the response of the microlayer to a decrease in wind stress appears to be slow in the absence of organized subsurface flows that form zones of convergence. Figure 2, for example, illustrates the time evolution of the surface microlayer during a period of decreasing wind speed at MVCO on Yearday 261 2002.

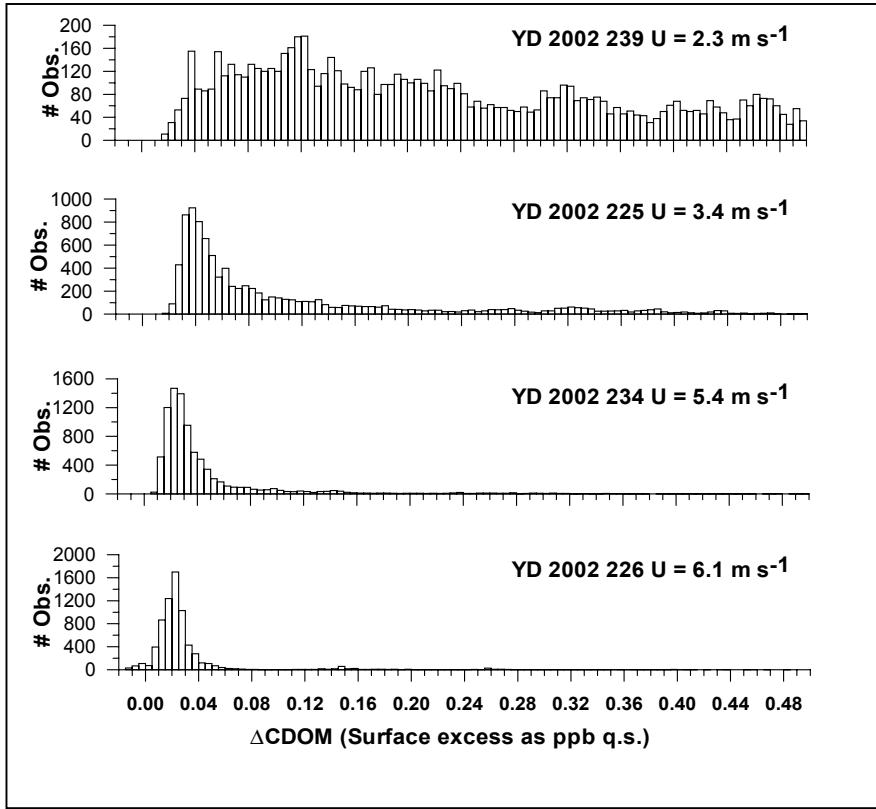


Figure 1: Histograms showing the distribution of surface excess colored dissolved organic matter (Δ CDOM) for four separate 4 hr SCIMS deployments at MVCO. Distributions are typically broad with high mean Δ CDOM at very low winds ($U = 2 \text{ m/s}$) and become increasingly narrow with lower means as winds increase ($U = 6 \text{ m/s}$). CDOM fluorescence is calibrated against quinine sulfate (q.s.) standards such that one CDOM fluorescence unit = 1 ppb q.s.

As winds decreased from 7 m/s to 3 m/s during the interval 261.55 – 261.74, Δ CDOM increased only slowly, while the surface tension and elasticity slowly decreased and increased respectively. This suggests that re-adsorption of surfactants from the underlying water via diffusive processes was slow. Dramatic increases in Δ CDOM beyond 261.74 correspond to development of a tidally driven convergence zone. The surface excess CDOM variations observed at low winds imply large changes in ripple damping, with expected reductions in degree of saturation, β , of 1-2 orders of magnitude at wavenumber $k = 400 \text{ rad/m}$ (Bock *et al.*, 1999). These reductions in turn imply strong effects on momentum and mass transfer during low wind episodes. In addition it is known that wave slope of ripples with wavenumbers $k > 400$ declines for Δ CDOM levels as low as 0.02-0.04 ppb q.s. at winds up to 6 m/s (Frew *et al.*, 2002b).

The SCIMS microlayer extracts are being analyzed using a variety of mass spectrometric techniques. A ‘quick look’ mode is used to initially screen samples for molecular weight range and prominent spectral features needing further investigation. In-source pyrolysis low voltage electron impact mass spectra of microlayers indicate up to 5x enrichments of lipoidal surfactants compared to subsurface samples. Ions diagnostic of various biopolymeric compound classes indicate 2x enrichments in some samples. Electrospray ionization spectra show a broad envelope of ions in the scan range of 100-1500 amu, representing primarily singly-charged (protonated or sodiated) parent ions, with a maximum abundance in the molecular weight range of 800-1100 amu. Several series of prominent ions appear to arise from highly oxygenated compounds. Multistage (MS^n) electrospray studies suggest that these compounds are polyethers and acetylated polyols. A more complete identification is being pursued using a combination of ionization modes (electron impact, chemical ionization and electrospray) and multistage (MS^n) mass spectral techniques.

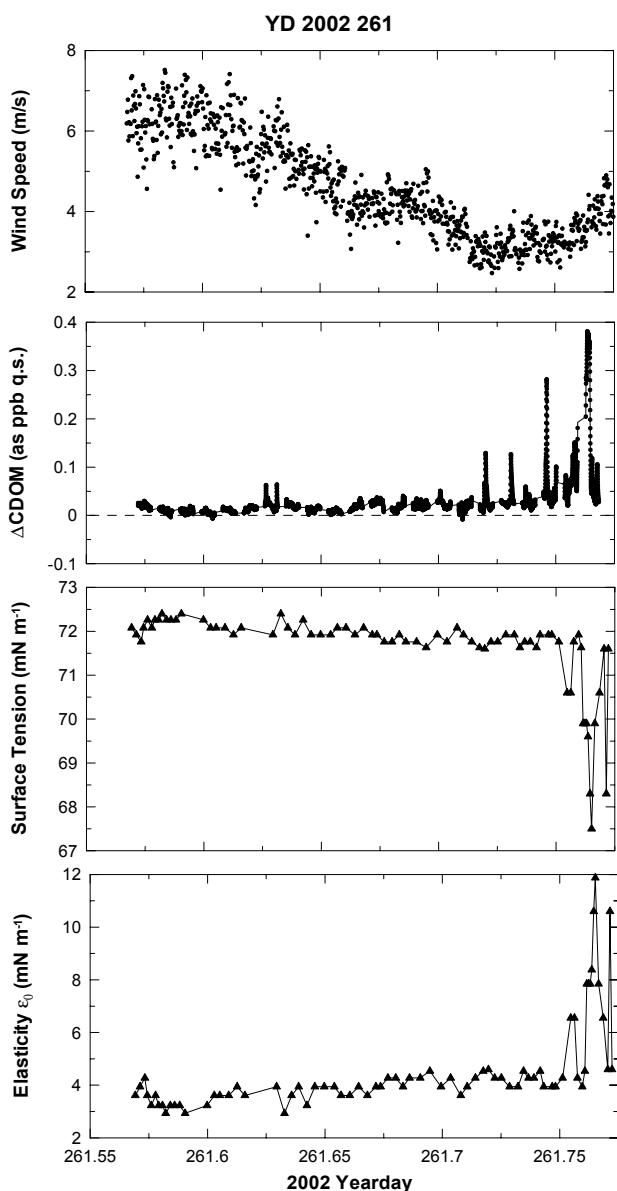


Figure 2: Time series data from SCIMS (YD 2002 261) showing the response of the microlayer during a 4-hr period of decreasing wind speed, with slowly increasing $\Delta CDOM$, decreasing surface tension and increasing elasticity. A tidally driven convergence zone encountered beyond time 261.74 showed strong $\Delta CDOM$ banding.

IMPACT/APPLICATIONS

SCIMS is providing new information on the surface microlayer, including film abundance and distributions in relation to physical forcing, the molecular identity and concentrations of organic compounds in the sea surface microlayer and better estimates of surface elasticity. The availability of such information during field studies will allow more detailed investigations of air-sea interactions and improved groundtruthing of microwave remote imagery. More rapid information acquisition will allow process studies of links between biology, surfactant production and film distributions, the role of hydrodynamic processes in film formation and dispersal, photochemical degradation processes in the microlayer, and the relative importance of insoluble lipid and soluble biopolymeric surfactants in determining sea surface viscoelasticity. Expected major applications include studies of the role of the marine microlayer in modulating small-scale waves and microwave scattering, microwave signatures of internal waves, wind stress-drag relationships, and turbulent surface renewal and air-sea gas exchange.

TRANSITIONS

None

RELATED PROJECTS

This project is closely related to my NOAA-funded effort to understand the role of wind stress, small scale waves, near-surface turbulence, and surface films in modulating air-sea gas exchange (with T. Hara, U. Schimpf, and B. Jähne) and to my NASA-funded effort to develop algorithms to quantify air-sea gas exchange using remotely-sensed surface roughness (with D. Glover). A collaboration with investigators (J. Edson and others) involved in the CBLAST-LOW initiative to model boundary layer fluxes is also ongoing.

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